

FORM PTO-1390 (Modified)  
(REV 11-98)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

65243-001

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/743545

INTERNATIONAL APPLICATION NO.

PCT/EP99/05409

INTERNATIONAL FILING DATE

28 July 1999 (28.07.99)

PRIORITY DATE CLAIMED

31 July 1998 (31.07.98)

TITLE OF INVENTION

DEVICE AND METHOD FOR THE VACUUM PLASMA PROCESSING OF OBJECTS

APPLICANT(S) FOR DO/EO/US

JUNG, Thomas

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau)
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau)
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409)
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

## Items 13 to 20 below concern document(s) or information included:

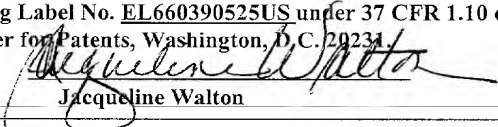
13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☒ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☒ Other items or information:

Marked up version of the PCT Application with the amendments made as described in the Preliminary Amendment

Clean copy of the translated PCT Application incorporating all noted amendments as described in the Preliminary amendment.

## CERTIFICATE OF EXPRESS MAILING

I hereby certify that the attached documents were deposited with the United States Postal Service "Express Mail Post Office to Addressee" Express Mailing Label No. EL660390525US under 37 CFR 1.10 on January 10, 2001 and addressed to BOX PCT, Assistant Commissioner for Patents, Washington, D.C. 20234.


  
Jacqueline Walton

U.S. APPLICATION NO. (IF KNOWN) SEE 37 CFR

INTERNATIONAL APPLICATION NO.

ATTORNEY'S DOCKET NUMBER

09/743545

PCT/EP99/05409

65243-001

21. The following fees are submitted:

**BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5) ) :**

- ☒ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO . . . . . \$1,000.00
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO . . . . . \$860.00
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . . \$710.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . \$690.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . \$100.00

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

\$1,000.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e))

\$0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	19 - 20 =	0	x \$18.00
Independent claims	2 - 3 =	0	x \$80.00

\$0.00

\$0.00

Multiple Dependent Claims (check if applicable). ☐

\$0.00

**TOTAL OF ABOVE CALCULATIONS =**

\$1,000.00

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). ☐

\$0.00

**SUBTOTAL =**

\$1,000.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +

\$0.00

**TOTAL NATIONAL FEE =**

\$1,000.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☐

\$0.00

**TOTAL FEES ENCLOSED =**

\$1,000.00

Amount to be:

refunded

\$

charged

\$

☒ A check in the amount of **\$1,000.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees.  
A duplicate copy of this sheet is enclosed.


☐ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **08-2789** A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

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NAME

22,180

REGISTRATION NUMBER

10 JANUARY 2001

DATE

525 Rec'd PCT/PTO 10 JAN 2001

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In Re Application of: Thomas Jung  
Int'l Serial No: PCT/EP99/05409  
Int'l Filing Date: 28 July 1999  
Attny Docket No: 65,243-001  
Title: DEVICE AND METHOD FOR COATING AND/OR  
SURFACE MODIFICATION OF OBJECTS BY MEANS OF  
A PLASMA

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

**BOX PCT**

Dear Sirs:

Prior to examination of the above-identified application, please amend the claims as follows:

**IN THE SPECIFICATION**

Please amend the specification as follows:

Page 1, before line 4 please insert the following heading - - BACKGROUND OF THE INVENTION- -

Page 1, before line 5 please insert the following heading- -1. Field of the Invention--.

Page 1, before line 15, please insert the following heading - -2. Description of the Prior Art- -

Page 2, before line 5, please insert the following heading - -SUMMARY OF THE INVENTION AND ADVANTAGES- -

Page 2, line 10, please delete "In accordance with the invention, this task is solved by the characteristics of Claim 1 for the device and the characteristics of Claim 11 for the method. Advantageous embodiments and further developments of the invention result from the use of the characteristics indicated in the subordinate claims."

Page 2, line 14, please insert the following - -BRIEF DESCRIPTION OF THE DRAWINGS- -.

Page 2, line 15, please insert the following paragraphs- -Figure 1 shows an example of a device in accordance with the invention with an inserted electrode for plasma generation, and

Figure 2 shows a second example of a device in accordance with the invention with an opening through which microwaves can be directed for plasma generation.- -

Page 2, before line 21 please insert the following heading - -DETAILED DESCRIPTION OF THE INVENTION- -

Page 2, line 22 please insert the following paragraphs- -Figure 1 represents a box structure 1 with rectangular cross section. An end face 8 is formed as an opening through which objects 2 are introduced and can be removed. Opening 8 can, as shown, be reclosed. The operating gas can be introduced into the flat structure 1 through opening 3 and can be removed again through the larger and diametrically oppositely arranged opening 4.

Electrode 5, which is in this case connected as an anode, is inserted via an additional opening 6'. Between anode 5 and the box structure 1 there is insulation, not shown, so that the potentials are separate from one another.

Page 3, line 1 please insert the following paragraphs- -Figure 2 shows as a cylindrical box structure 1 in which several objects 2 are arranged on a support 7 insulated from the box structure 1. The upper face is again formed as a cover 8, which can be removed and reattached.

There is an opening 6 in cover 8, through which microwaves can be directed into the interior of the box structure 1 and a plasma can be generated.

In this example there are two openings 3 in the outer jacket surface, through which operating gas can be introduced into the interior of the box structure 1. The gas can be removed through opening 4, which in this example is combined with a support, from the box structure 1.- -

Page 10, line 15, please delete "The organization of possible examples of a device in accordance with the invention is described in more detail below."

Page 10, line 17, please delete "Here:"

Page 10, line 18, please delete "Figure 1 shows an example of a device in accordance with the invention with an inserted electrode for plasma generation, and

Page 10, line 20 please delete "Figure 2 shows a second example of a device in accordance with the invention with an opening through which microwaves can be directed for plasma generation."

Page 10, line 23, please delete "Figure 1 represents a box structure 1 with rectangular cross section. An end face 8 is formed as an opening through which objects 2 are introduced and can be removed. Opening 8 can, as shown, be recessed. The operating gas can be introduced into the flat structure 1 through opening 3 and can be removed again through the larger and diametrically oppositely arranged opening 4."

Page 10, line 28 please delete "Electrode 5, which is in this case connected as an anode, is inserted via an additional opening 6'. Between anode 5 and the box structure 1 there is insulation, not shown, so that the potentials are separate from one another."

Page 11, line 1 please delete "Figure 2 shows a cylindrical box structure 1, in which again several objects 2 are arranged on a support 7 insulated from the box structure 1. The upper face is again formed as a cover 8, which can be removed and reattached."

Page 11, line 4 please delete "There is an opening 6 in cover 8, through which microwaves can be directed into the interior of the box structure 1 and a plasma can be generated."

Page 11, line 6 please delete "In this example there are two openings 3 in the outer jacket surface, through which operating gas can be introduced into the interior of the box structure 1. The gas can be removed through opening 4, which in this example is combined with a support, from the box structure 1."

### **IN THE SUMMARY**

Please preliminary amend the Summary as follows:

Page 14 line 1, please delete "Summary" and insert - -ABSTRACT OF THE DISCLOSURE- -.

### **IN THE CLAIMS:**

Please preliminary amend the claims as follows:

Claim 4, line 1, after "in" please delete "one of Claims 1-3," and insert - -claim 1- -.

Claim 5, line 1, after "in" please delete "one of Claims 1-4," and insert - -claim 1- -.

Claim 6, line 1, after "in" please delete "one of Claims 1-5," and insert - -claim 1- -.

Claim 7, line 1, after "in" please delete "one of Claims 1-6," and insert - -claim 1- -.

Claim 8, line 1, after "in" please delete "one of Claims 1-7," and insert - -claim 1- -.

Claim 9, line 1, after "in" please delete "one of Claims 1-8," and insert - -claim 1- -.

Claim 9, line 2, after "opening" please cancel "(5)" and insert - -(4)- -.

Claim 10, line 1, after "in" please delete "one of Claims 1-9," and insert - -claim 1- -.

Claim 11, line 2, after "in" please delete "one of Claims 1-10," and insert - -claim 1- -.

Claim 13, line 1, after "in" please delete "Claim 11 or 12", and insert - -claim 11- -.

Claim 14, line 1, after "in" please delete "one of Claims 11-13," and insert - -claim 11- -.

Claim 15, line 1, after "in" please delete "one of Claims 12-14," and insert - -claim 12- -.

Claim 16, line 1, after "in" please delete "one of Claims 12-15," and insert - -claim 12- -.

Claim 17, line 1, after "in" please delete "one of Claims 12-16," and insert - -claim 12- -.

Claim 18, line 1, after "in" please delete "one of Claims 12-17," and insert - -claim 12- -.

Claim 19, line 1, after "in" please delete "one of Claims 11-18," and insert - -claim 11- -.

### **REMARKS**

The specification and claims 1-19 have been amended to conform to United States Practice and to eliminate multiple dependency.

Applicant provides herewith 3 separate versions of the PCT Application. The versions are as follows:

1. Translated PCT Application as originally filed in the European Patent Office
2. Marked up version of the same PCT Application with the amendments made as instructed by this Preliminary Amendment.
3. Clean copy of the PCT Application incorporating all noted amendments, which applicant has recommended through this Preliminary Amendment.

Early and favorable consideration is respectfully solicited.

**Respectfully submitted,**

**HOWARD & HOWARD ATTORNEYS, P.C.**

1-10-01  
**Date**



**Harold W. Milton, Reg. No. 22,180**  
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**Enclosures**

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525 Rec'd PCT/PTO 10 JAN 2001

Clean copy of substitute specification and claim.

-1-

## **DEVICE AND METHOD FOR COATING AND/OR SURFACE MODIFICATION OF OBJECTS IN A VACUUM BY MEANS OF A PLASMA**

### **BACKGROUND OF THE INVENTION**

5

#### **1. Field of the Invention**

The invention concerns a device and a method for coating and/or surface modification of objects in a vacuum using a plasma, in which there is the possibility of coating or modifying variform objects on all sides without a large expenditure for plant and process engineering being required. Besides coating or modification, it is also easily possible to conduct cleaning, etching and/or activation to improve, for example, the adhesion of coatings that may be subsequently applied.

Besides the modification of regions of objects that are close to the surface it is also possible by means of the invention to apply particularly microscopically dense metal coatings or compound layers that have low roughness.

15

#### **2. Description of the Prior Art**

The deposition of coatings on objects using a planar direct current magnetron is known from G. Kienel, Vacuum Coating [in German], Volume 2, VDI Verlag GmbH, Düsseldorf, 1993, pp. 160-161.

20

Such a solution, however, enables the coating of objects that is to be carried out spatially in three dimensions only if the objects are moved at the same time, which can be realized only with great difficulty and at great costs, if at all, especially in the vacuum chambers that are required for this. If such objects have undercut areas, these normally cannot be coated.

25

In addition, harmful effects from residual gases have to be avoided by producing a high vacuum, which either greatly increases the time needed to produce the vacuum, or requires costly vacuum locks or costly high vacuum pumps.

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Another disadvantage is that larger surfaces are parasitically coated, which leads to high losses of the coating material, which has an adverse effect in particular for expensive coating materials such as noble metals. In addition, costs for cleaning are higher because of the parasitic coatings in the chamber and the elements found there.



The amount of coating material that can be applied to the corresponding objects is correspondingly limited, so that a relatively frequent interruption of the coating process is necessary for the necessary changeover of the target.

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## SUMMARY OF THE INVENTION AND ADVANTAGES

Thus, it is a task of the invention to propose a device and a corresponding method with which surface modification and/or coating of objects of quite various designs on all sides and optionally even on undercut surface regions can be achieved at low cost for plant engineering process engineering and other expenses.

10

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows an example of a device in accordance with the invention with an inserted electrode for plasma generation, and

15

Figure 2 shows a second example of a device in accordance with the invention with an opening through which microwaves can be directed for plasma generation.

## DETAILED DESCRIPTION OF THE INVENTION

20

Figure 1 represents a box structure 1 with rectangular cross section. An end face 8 is formed as an opening through which objects 2 are introduced and can be removed. Opening 8 can, as shown, be reclosed. The operating gas can be introduced into the flat structure 1 through opening 3 and can be removed again through the larger and diametrically oppositely arranged opening 4.

25

Electrode 5, which is in this case connected as an anode, is inserted via an additional opening 6'. Between anode 5 and the box structure 1 there is insulation, not shown, so that the potentials are separate from one another.

30

Figure 2 shows as a cylindrical box structure 1, in which several objects 2 are arranged on a support 7 insulated from the box structure 1. The upper face is again formed as a cover 8, which can be removed and reattached.

There is an opening 6 in cover 8, through which microwaves can be directed into the interior of the box structure 1 and a plasma can be generated.

In this example there are two openings 3 in the outer jacket surface, through which operating gas can be introduced into the interior of the box structure 1. The gas can be removed through opening 4, which in this example is combined with a support, from the box structure 1.

5           The device in accordance with the invention can correspondingly be modified for the coating, already mentioned at the start in the description, of objects with metals, metal alloys or various metal compounds like metal nitrides or metal oxides or alternatively and cumulatively for this on the surfaces, so that, for example, the adhesion properties of coatings that are to be applied later can be improved. Here a box structure, which can have, for example, the form of a rectangle, cube or cylinder of an electrically conductive material is used. The box structure can, by itself, represent a vacuum chamber, which is used by connecting the appropriate pumps and valves in combination, with the technical elements to be used subsequently. However, there is also the possibility of inserting such a box structure into a traditional vacuum chamber and operating there in accordance with the invention.

          The objects that are to be coated or modified are inserted into the box structure, namely so that direct contact between the objects and the inner wall is avoided and, apart from that, an electrical insulation is used as support for the objects. The objects can be inserted into the box structure preferably via various openings, so that the objects are surrounded on all sides. The box structure can, however, also consist of two parts, with one part forming a cover that can be positioned on the lower part.

          At least the inner wall should consist of a material that is suitable for the coating. Of course, it is also possible for the entire box structure to be formed from a material suitable for the coating or for flat targets of a coating material to be arranged on the inner walls of the box structure.

          In addition, openings for feed and withdrawal of the working gas as well as at least one opening through which the energy to produce a glow discharge can be introduced into the box structure are necessary.

For the modification or coating the box structure is charged to an electrically negative potential with respect to the plasma generated with the glow discharge.

The plasma generation that is brought about by a glow discharge can take place in various ways. For this there is on the one hand the possibility of inserting an electrode through an opening into the interior of the box structure and supplying direct or alternating current to the electrode. If direct current is supplied, the electrode is connected as the anode. The correspondingly supplied alternating current can be low frequency, medium frequency or high frequency.

Another possibility for generating the plasma is to direct microwaves through an opening into the interior of the box structure and thus to generate the plasma.

Since the box structure has a negative electrical potential compared to the plasma, material can be stripped at the inner surface through the appearance of high energy positive ions from the plasma (cathode sputtering), and this material is then deposited on the objects. However, a sufficient difference of potential must be established for this. If an appropriate potential difference has not been reached, no or nearly no material will be stripped away and there will only be a modification in the subsurface region of the objects held in the box structure. The objects can consist of quite various materials such as metal, plastic or ceramic.

By simply increasing the difference of potentials between the box structure and the plasma it is possible to initiate coating of the objects, in addition to modification. Through the appropriate stripping of material at all inner walls of the box structure coating of any three dimensionally shaped object on all sides is possible without additional manipulation of the objects and it is also possible to coat undercut regions, with increased working pressure, which leads to dispersed distribution of the stripped material components, having a favorable effect. Thus, uniform and nearly simultaneous modification and/or coating of objects can be achieved.

The coating material that is not directly deposited on the surface of the object is essentially redeposited on the inner surface of the box structure and thus is not lost to the coating process. Since dispersed coatings are deposited only on relatively

small internal fittings in the box structure such as, for example, the support on which the objects are held, the cleaning cost is reduced considerably compared to the traditional solutions.

5 The adsorbate layers that, as is well known, form in such processes and have an adverse effect on the quality of the layer and layer adhesion in vacuum coating processes through their desorption during coating can be counteracted very effectively through ion bombardment removal. For this the interior of the box structure can be cleaned relatively shortly before the actual coating with a low plasma power, low negative potential on the box structure and/or by providing an  
10 elevated operating pressure, so that no additional technical requirements have to be met to remove the adsorbate layers and the adsorbate after being separated can easily be drawn out with the operating gas.

With the device in accordance with the invention there is also the possibility of already removing a large proportion of the adsorbate layers before initiating the  
15 glow discharge and plasma generation with the introduction and evacuation of a clean dry operating gas during the evacuation phase. Relatively little operating gas is needed for this, since the box structure and its inner surface can be relatively small compared to the inner surface of the traditional vacuum coating chambers, for equal volumes of objects that are to be coated.

20 Through the ion bombardment the inner surface of the box structure can be heated in a simple manner and way and without additional technical cost, so that the desorption of the adsorbate layers can be considerably accelerated.

If the box structure is used in a larger vacuum chamber and accordingly does not itself act as a vacuum chamber, there still remains the effect that the gas flow in  
25 the box structure cannot force any desorbable gases from the walls of the larger vacuum chamber into the box structure due to the relatively small free cross section of its openings.

Since the cleaning of adsorbate layers by ion bombardment and gas flow in the interior space of the box structure is very effective, and the necessary operating  
30 pressure during the actual coating lies in the range of a coarse/fine vacuum, a high vacuum pump with the correspondingly high cost is not necessary.

Compared to the known solution of coating with magnetron sources, the solution in accordance with the invention offers another advantage, which is that considerably more coating material is available than is the case with the targets that are used in the known solution. Since the entire inner surface of the box shaped material consists of coating material, or appropriately dimensioned flat targets of such a coating material are arranged there, the stock of coating material is considerably larger and the process has to be interrupted correspondingly less often for recharging with coating material. In addition, the plasma parameters do not unduly change even when severe stripping of coating material has occurred. In addition, there is no limitation due to thermal resistance caused by a great target thickness.

The box structure can, in combination with the pressure of the operating gas, be dimensioned so that the discharge produced as a consequence of the introduced energy has the character of a hollow cathode glow discharge, so that a particularly high plasma density and accordingly a high coating rate can be achieved without expensive permanent magnets being necessary, as is the case with magnetrons. Here the condition  $\text{pressure} \cdot \text{tube inside diameter} = 133.3 \text{ Pa} \cdot \text{cm}$  with a tolerance range of a maximum of  $13.33\text{--}133.3 \text{ Pa} \cdot \text{cm}$  that was mentioned by M. v. Ardenne in Effects of Physics [in German], Verlag Harry Deutsch, Thun, Frankfurt/Main, 1990, can be correspondingly taken into consideration for the development of a hollow cathode discharge when the relevant clear width of the box structure is used for the tube inside diameter.

Since in accordance with the invention modification and coating can be carried out at relatively low temperatures, there is also the possibility, and this has a very favorable effect, that the box structure can be provided with cooling, preferably water cooling.

As already noted, the difference of potentials between the generated plasma and the box structure can be specifically affected and can be established in the range between 100 to 1000 V. Here the smaller voltage values are sufficient for modification and the higher voltage values are necessary for applying a coating.

The pressure in the box structure can be specifically established in the range between  $10^{-3}$  to 10 mbar.

The opening for withdrawal of the operating gas has a size between a few  $\text{cm}^2$  up to about  $100 \text{ cm}^2$  and it is a good idea to dimension the other openings in the box structure so that their sum is less than the size of the withdrawal opening.

The box structure can have a clear width in the range between 1 cm and 1 m and should have a size at least 1.2 times that of the objects and should be a maximum of 10 times as large as the objects. The objects that are to be modified or coated should fill the interior of the box structure to a volume of about 0.1% to 30%. The objects in the box structure should be electrically isolated from the structure, for example on one or more supports, and should have a distance of at least 0.1 to a maximum of 10 cm from the inner wall of the box structure.

Various metals can be used, for example, aluminum, titanium, or alloys of these. However, it is also possible to use metal compounds such as titanium nitride or indium-tin oxide.

The operating gas, especially for flushing and cleaning, can be a clean dry inert gas, for example argon. However, an operating gas mixture of an inert gas and a reactive gas can be used for coating. One such operating gas is, for example, argon and nitrogen, so that nitride layers can be deposited on the objects.

The gas flow can be adjusted to a minimum of  $10 \text{ cm}^3/\text{min}[\text{STP}]$  (cubic centimeters per minute at standard temperature and pressure) and a maximum of  $1000 \text{ cm}^3/\text{min}[\text{STP}]$ .

If only a very small coating or no coating at all is intended to be applied, the potential difference between the plasma and the box structure should be set to be under 200 V and/or the pressure should be increased by at least a factor of three. With adjustment of this kind a surface modification, as already noted in general, can be carried out.

The device in accordance with the invention can also be used to produce composite structures. For this it is provided that a solid powder is supplied through one of the openings that are present or through an opening specifically made for this. It is also possible to place the solid powder in the device in a container. The particles

of the solid powder preferably have a size from  $10^{-4}$  to  $10^{-9}$  m. Basically all known hard materials are possibilities as solid particles. Examples are high-melting metal oxides like corundum or titanium oxide. Diamond graphite or nitrides can also be used. In accordance with the method, when the powder is introduced via an opening,  
5 it is mixed into the inert gas stream. If the powder is supplied in a container, automatic turbulent mixing takes place due to the applied vacuum. The particles are then deposited on the surface that is to be coated.

The mode of operation in accordance with the invention will be described first below, in general form and then in more detail using two specific examples.

10 After putting the objects in the box structure, the box structure or the surrounding vacuum chamber is evacuated out by means of a vacuum pump and at the same time or shortly afterwards flushing with the operating gas is carried out.

If a sufficiently low pressure (1-10 mbar) has been achieved, the box structure is charged to a negative potential with respect to the plasma and the glow  
15 discharge is initiated by the supply of energy. The ion-supported desorption of the adsorbate layers takes place by means of this.

After sufficient cleaning the pressure is reduced to a pressure in the range between 0.001 and 1 mbar by reducing the feed of operating gas and the potential difference between the box structure and the plasma is increased. This can take  
20 place, for example, by increasing the negative potential, thus a higher negative voltage is supplied to the box structure. Due to this, material of the coating material is stripped from the inner wall of the flat structure and the objects in the structure are correspondingly coated. In each case according to the coating to be applied a pure inert gas or an inert gas-reactive gas mixture can be used as the operating gas. The  
25 fraction of reactive gas, however, must be established in correspondence with the desired layer structure.

Then the glow discharge can be switched off, the supply of operating gas in the pump disconnected and the vacuum chamber or the box structure flooded and after opening the box the modified or coated objects are removed.

The following Examples 1 and 2 are intended to describe on the one hand coating of objects with copper and on the other coating with titanium nitride in more specific detail.

5        Example 1

The objects are put into the box structure, which is shaped as a tube, is situated in a vacuum vessel, and consists of block copper. For evacuation of the vacuum vessel the vacuum pump is connected. At the same time flushing with argon at about  $100 \text{ cm}^3/\text{min}[\text{STP}]$  is carried out.

10        Upon reaching a pressure of 5 mbar the box structure is charged to a negative potential of 300 V compared to a rod shaped anode inserted into the box structure and the glow discharge is initiated. This causes the ion-supported desorption of the adsorbate layers from the inner wall of the box structure.

15        After sufficient cleaning the pressure is reduced to the operating pressure of 0.5 mbar by reducing the feed of gas and the potential of the box structure is set to -500 V, so that coating of the objects with copper takes place.

20        After 10 min coating time the glow discharge is switched off by disconnecting the supply of current and the argon supply is turned off. The pump is disconnected and the box structure is aerated. The vacuum vessel and box structure are opened and the coated objects are removed.

Example 2

25        The objects are put into the box structure. The box has the shape of a rectangular parallelepiped, consists of aluminum and is itself the vacuum vessel, which is coated nearly completely on its inside with titanium sheets ("targets"). The box structure has a short tubular stub in its wall, to which a microwave source is connected.

30        The vacuum pump is switched on for evacuation of the box. Shortly after that argon is supplied for flushing at about  $300 \text{ cm}^3/\text{min}[\text{STP}]$ . Upon reaching a pressure of 10 mbar the box structure is charged to a negative potential of 250 V and the glow discharge is initiated by turning on the microwave source.



After 3 min cleaning the pressure is reduced to 0.3 mbar by reducing the gas supply, and the objects are supplied with a potential of  $-500$  V, through which surface cleaning takes place. Then 10% nitrogen is added to the argon and the potential of the box structure is set to  $-600$  V, so that coating of the objects with titanium nitride takes place.

After 15 min of coating the glow discharge is turned off and the operating gas supply stopped. The pump is isolated by a valve and the box is aerated. The box is opened and the objects are removed.

Claims

1. A device for coating and/or surface modification of objects in a vacuum, by means of a plasma, which is characterized by the fact that a box structure (1) of an electrically conductive material forms a vacuum chamber or can  
5 be inserted into a vacuum chamber, into which objects (2) are inserted into the box structure (1) through at least one closable opening (8) at a distance from the inner wall, at least one opening (3) for supply and at least one opening (4) for removal of operating gas and an opening (6,6') for introduction of energy for generation of a glow discharge are present, and the box structure (1) has a potential that is  
10 electrically negative with respect to the plasma generated by the glow discharge.

2. A device as in claim 1, which is characterized by the fact that an electrode (5), to which a DC or AC voltage is applied for plasma generation, is inserted into the box structure (1) through an opening (6').  
15

3. A device as in claim 1, which is characterized by the fact that microwaves for plasma generation are directed into the interior of the box structure through opening (6).  
20

4. A device as in claim 1, which is characterized by the fact that the objects (2) are arranged in electrically isolated fashion from the box structure (1).  
25

5. A device as in claim 1, which is characterized by the fact that the objects (2) are supplied with a settable electrical potential.  
30

6. A device claim 1, which is characterized by the fact that the inner wall of the box structure (1) or the box structure (1) is formed of a coating material or is arranged there as a flat target.

7. A device as in claim 1, which is characterized by the fact that the box structure (1) is cooled.

8. A device as in claim 1, which is characterized by the fact that the clear width of the box structure (1) is at least 1.2 times that of the objects (2) and the objects (2) fill the space available in the box structure (1) to a percentage of 0.1% to 30%.

5

9. A device as in claim 1, which is characterized by the fact that the size of the withdrawal opening (4) is larger than the sum of the larger of the other openings (3,6,6') of the box structure (1).

10

10. A device as in claim 1, which is characterized by the fact that the box structure (1) or its inner surface consists of a metal, a metal alloy or a metal compound.

15

11. A method for coating and/or modification of the surfaces of objects with a device as in claim 1, which is characterized by the fact that after evacuation to a sufficiently low pressure and flushing with an operating gas a plasma is generated in the box structure (1), where the plasma power and the negative potential of the box structure (1) are set so that modification of the surface and/or, through material stripping from the inner wall of the box structure (1), coating of the surface of the object (2) is carried out.

20

25

12. A method as in claim 11, which is characterized by the fact that before modification or coating an ion-supported desorption of deposited adsorbate layers is carried out with applied negative potential applied to the box structure (1) and glow discharge initiated.

13. A method as in claim 11, which is characterized by the fact that reactive gas is supplied during the coating.

14. A method as in claim 11, which is characterized by the fact that solid powder is introduced into the box structure and/or is made available in a container arranged there and the solid powder is deposited on the surface (2) of the objects.

5 15. A method as in claim 12, which is characterized by the fact that the potential difference between the box structure (1) and the plasma is set in the range between 100-1000 V.

10 16. A method as in claim 12, which is characterized by the fact that the operating gas is adjusted to a volume flow of 10-1000 cm<sup>3</sup>/min[STP].

15 17. A method as in claim 12, which is characterized by the fact that for surface modification the potential difference between the plasma and the box structure (1) is adjusted to less than 200 V and/or the pressure is increased by at least threefold.

18. A method as in claim 12, which is characterized by the fact that a hollow cathode flow discharge is formed in the box structure (1).

20 19. A method as in claim 11, which is characterized by the fact that an inner gas, reactive gas or a mixture of inert and reactive gas is introduced in a timewise defined fashion as the working gas into the box structure (1).

# ABSTRACT OF THE DISCLOSURE

The invention concerns a device and a method for coating and/or surface modification of objects in a vacuum using a plasma, where there is the possibility of coating or modifying variform objects on all sides without a large expense for plant or process engineering being necessary. In accordance with the invention, a box structure (1) of an electrically conductive material that forms a vacuum chamber or can be inserted into a vacuum chamber is used. Objects (2) can be introduced into the box structure to at least one closable opening (8) at a distance from the inner wall. In addition, there are at least one opening (3) for supply and at least one opening (4) for removal of the operating gas as well as one opening (6,6') for introduction of energy for generation of a glow discharge and the box structure (1) has a potential that is electrically negative with respect to the plasma generated by the glow discharge.

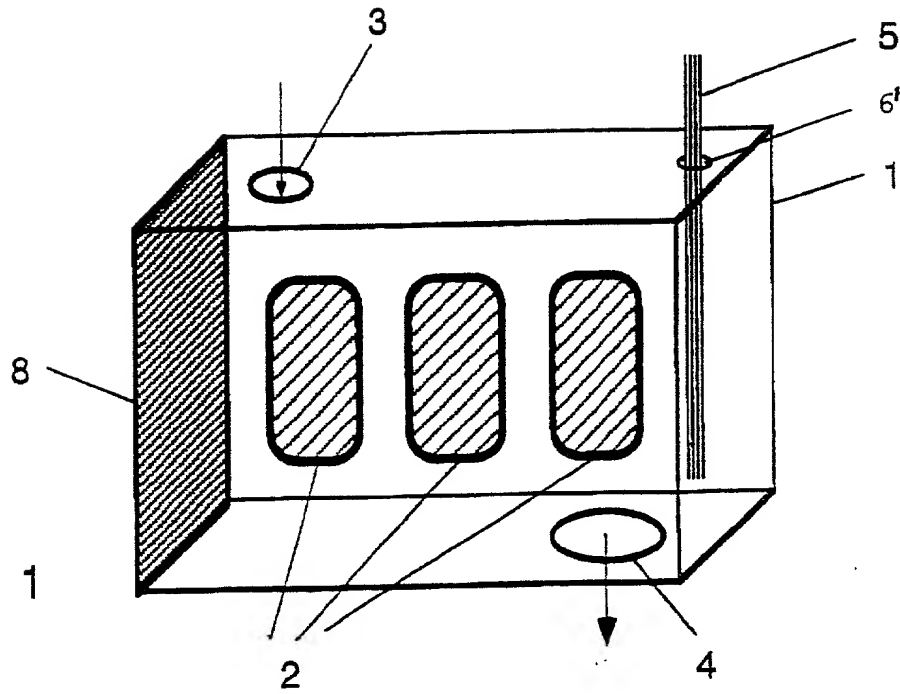


Fig. 1

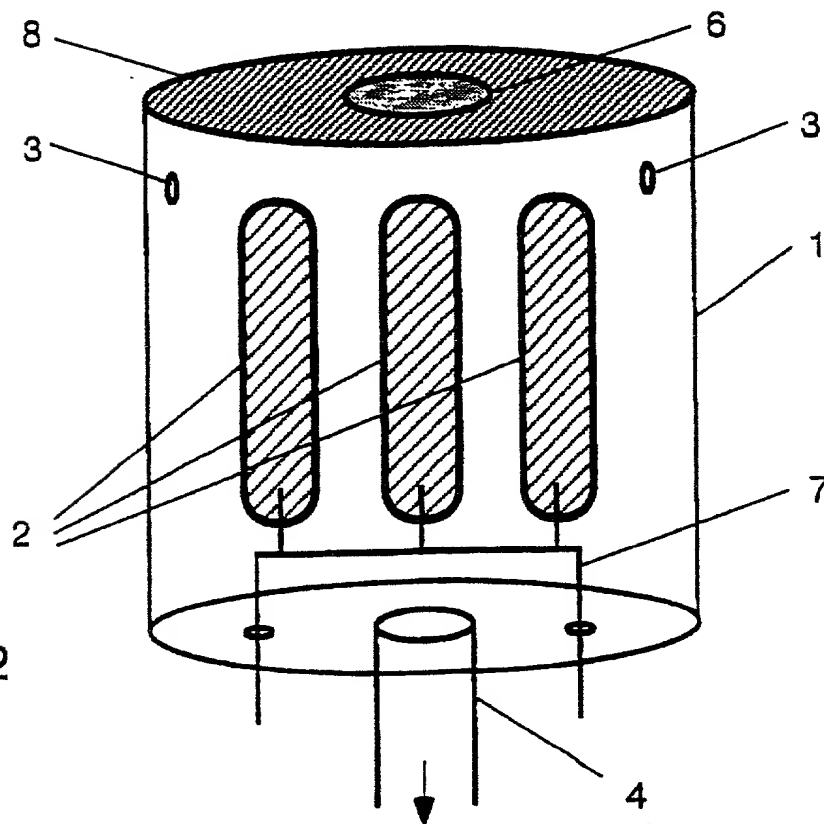


Fig. 2

Translation of Original Application

-1-

**DEVICE AND METHOD FOR COATING AND/OR SURFACE  
MODIFICATION OF OBJECTS IN A VACUUM BY MEANS OF A PLASMA**

The invention concerns a device and a method for coating and/or surface  
5 modification of objects in a vacuum using a plasma, in which there is the possibility  
of coating or modifying variform objects on all sides without a large expenditure for  
plant and process engineering being required. Besides coating or modification, it is  
also easily possible to conduct cleaning, etching and/or activation to improve, for  
example, the adhesion of coatings that may be subsequently applied.

10 Besides the modification of regions of objects that are close to the surface it  
is also possible by means of the invention to apply particularly microscopically  
dense metal coatings or compound layers that have low roughness.

The deposition of coatings on objects using a planar direct current magnetron  
is known from G. Kienel, Vacuum Coating [in German], Volume 2, VDI Verlag  
15 GmbH, Düsseldorf, 1993, pp. 160-161.

Such a solution, however, enables the coating of objects that is to be carried  
out spatially in three dimensions only if the objects are moved at the same time,  
which can be realized only with great difficulty and at great costs, if at all, especially  
in the vacuum chambers that are required for this. If such objects have undercut  
20 areas, these normally cannot be coated.

In addition, harmful effects from residual gases have to be avoided by  
producing a high vacuum, which either greatly increases the time needed to produce  
the vacuum, or requires costly vacuum locks or costly high vacuum pumps.

Another disadvantage is that larger surfaces are parasitically coated, which  
25 leads to high losses of the coating material, which has an adverse effect in particular  
for expensive coating materials such as noble metals. In addition, costs for cleaning  
are higher because of the parasitic coatings in the chamber and the elements found  
there.

The amount of coating material that can be applied to the corresponding  
30 objects is correspondingly limited, so that a relatively frequent interruption of the  
coating process is necessary for the necessary changeover of the target.

Thus, it is a task of the invention to propose a device and a corresponding method with which surface modification and/or coating of objects of quite various designs on all sides and optionally even on undercut surface regions can be achieved at low cost for plant engineering process engineering and other expenses.

5 In accordance with the invention, this task is solved by the characteristics of Claim 1 for the device and the characteristics of Claim 11 for the method. Advantageous embodiments and further developments of the invention result from the use of the characteristics indicated in the subordinate claims.

10 The device in accordance with the invention can correspondingly be modified for the coating, already mentioned at the start in the description, of objects with metals, metal alloys or various metal compounds like metal nitrides or metal oxides or alternatively and cumulatively for this on the surfaces, so that, for example, the adhesion properties of coatings that are to be applied later can be improved. Here a box structure, which can have, for example, the form of a  
15 rectangle, cube or cylinder of an electrically conductive material is used. The box structure can, by itself, represent a vacuum chamber, which is used by connecting the appropriate pumps and valves in combination, with the technical elements to be used subsequently. However, there is also the possibility of inserting such a box structure into a traditional vacuum chamber and operating there in accordance with  
20 the invention.

The objects that are to be coated or modified are inserted into the box structure, namely so that direct contact between the objects and the inner wall is avoided and, apart from that, an electrical insulation is used as support for the objects. The objects can be inserted into the box structure preferably via various  
25 openings, so that the objects are surrounded on all sides. The box structure can, however, also consist of two parts, with one part forming a cover that can be positioned on the lower part.

At least the inner wall should consist of a material that is suitable for the coating. Of course, it is also possible for the entire box structure to be formed from a  
30 material suitable for the coating or for flat targets of a coating material to be arranged on the inner walls of the box structure.



In addition, openings for feed and withdrawal of the working gas as well as at least one opening through which the energy to produce a glow discharge can be introduced into the box structure are necessary.

For the modification or coating the box structure is charged to an electrically  
5 negative potential with respect to the plasma generated with the glow discharge.

The plasma generation that is brought about by a glow discharge can take place in various ways. For this there is on the one hand the possibility of inserting an electrode through an opening into the interior of the box structure and supplying direct or alternating current to the electrode. If direct current is supplied, the  
10 electrode is connected as the anode. The correspondingly supplied alternating current can be low frequency, medium frequency or high frequency.

Another possibility for generating the plasma is to direct microwaves through an opening into the interior of the box structure and thus to generate the plasma.

15 Since the box structure has a negative electrical potential compared to the plasma, material can be stripped at the inner surface through the appearance of high energy positive ions from the plasma (cathode sputtering), and this material is then deposited on the objects. However, a sufficient difference of potential must be established for this. If an appropriate potential difference has not been reached, no or  
20 nearly no material will be stripped away and there will only be a modification in the subsurface region of the objects held in the box structure. The objects can consist of quite various materials such as metal, plastic or ceramic.

By simply increasing the difference of potentials between the box structure and the plasma it is possible to initiate coating of the objects, in addition to  
25 modification. Through the appropriate stripping of material at all inner walls of the box structure coating of any three dimensionally shaped object on all sides is possible without additional manipulation of the objects and it is also possible to coat undercut regions, with increased working pressure, which leads to dispersed distribution of the stripped material components, having a favorable effect. Thus,  
30 uniform and nearly simultaneous modification and/or coating of objects can be achieved.

The coating material that is not directly deposited on the surface of the object is essentially redeposited on the inner surface of the box structure and thus is not lost to the coating process. Since dispersed coatings are deposited only on relatively small internal fittings in the box structure such as, for example, the support on which the objects are held, the cleaning cost is reduced considerably compared to the traditional solutions.

The adsorbate layers that, as is well known, form in such processes and have an adverse effect on the quality of the layer and layer adhesion in vacuum coating processes through their desorption during coating can be counteracted very effectively through ion bombardment removal. For this the interior of the box structure can be cleaned relatively shortly before the actual coating with a low plasma power, low negative potential on the box structure and/or by providing an elevated operating pressure, so that no additional technical requirements have to be met to remove the adsorbate layers and the adsorbate after being separated can easily be drawn out with the operating gas.

With the device in accordance with the invention there is also the possibility of already removing a large proportion of the adsorbate layers before initiating the glow discharge and plasma generation with the introduction and evacuation of a clean dry operating gas during the evacuation phase. Relatively little operating gas is needed for this, since the box structure and its inner surface can be relatively small compared to the inner surface of the traditional vacuum coating chambers, for equal volumes of objects that are to be coated.

Through the ion bombardment the inner surface of the box structure can be heated in a simple manner and way and without additional technical cost, so that the desorption of the adsorbate layers can be considerably accelerated.

If the box structure is used in a larger vacuum chamber and accordingly does not itself act as a vacuum chamber, there still remains the effect that the gas flow in the box structure cannot force any desorbable gases from the walls of the larger vacuum chamber into the box structure due to the relatively small free cross section of its openings.

Since the cleaning of adsorbate layers by ion bombardment and gas flow in the interior space of the box structure is very effective, and the necessary operating pressure during the actual coating lies in the range of a coarse/fine vacuum, a high vacuum pump with the correspondingly high cost is not necessary.

5 Compared to the known solution of coating with magnetron sources, the solution in accordance with the invention offers another advantage, which is that considerably more coating material is available than is the case with the targets that are used in the known solution. Since the entire inner surface of the box shaped material consists of coating material, or appropriately dimensioned flat targets of  
10 such a coating material are arranged there, the stock of coating material is considerably larger and the process has to be interrupted correspondingly less often for recharging with coating material. In addition, the plasma parameters do not unduly change even when severe stripping of coating material has occurred. In addition, there is no limitation due to thermal resistance caused by a great target  
15 thickness.

The box structure can, in combination with the pressure of the operating gas, be dimensioned so that the discharge produced as a consequence of the introduced energy has the character of a hollow cathode glow discharge, so that a particularly high plasma density and accordingly a high coating rate can be achieved without  
20 expensive permanent magnets being necessary, as is the case with magnetrons. Here the condition  $\text{pressure} \cdot \text{tube inside diameter} = 133.3 \text{ Pa} \cdot \text{cm}$  with a tolerance range of a maximum of  $13.33\text{-}133.3 \text{ Pa} \cdot \text{cm}$  that was mentioned by M. v. Ardenne in Effects of Physics [in German], Verlag Harry Deutsch, Thun, Frankfurt/Main, 1990, can be correspondingly taken into consideration for the development of a hollow cathode  
25 discharge when the relevant clear width of the box structure is used for the tube inside diameter.

Since in accordance with the invention modification and coating can be carried out at relatively low temperatures, there is also the possibility, and this has a very favorable effect, that the box structure can be provided with cooling, preferably  
30 water cooling.

As already noted, the difference of potentials between the generated plasma and the box structure can be specifically affected and can be established in the range between 100 to 1000 V. Here the smaller voltage values are sufficient for modification and the higher voltage values are necessary for applying a coating.

- 5           The pressure in the box structure can be specifically established in the range between  $10^{-3}$  to 10 mbar.

The opening for withdrawal of the operating gas has a size between a few  $\text{cm}^2$  up to about  $100 \text{ cm}^2$  and it is a good idea to dimension the other openings in the box structure so that their sum is less than the size of the withdrawal opening.

- 10           The box structure can have a clear width in the range between 1 cm and 1 m and should have a size at least 1.2 times that of the objects and should be a maximum of 10 times as large as the objects. The objects that are to be modified or coated should fill the interior of the box structure to a volume of about 0.1% to 30%. The objects in the box structure should be electrically isolated from the structure, for  
15           example on one or more supports, and should have a distance of at least 0.1 to a maximum of 10 cm from the inner wall of the box structure.

Various metals can be used, for example, aluminum, titanium, or alloys of these. However, it is also possible to use metal compounds such as titanium nitride or indium-tin oxide.

- 20           The operating gas, especially for flushing and cleaning, can be a clean dry inert gas, for example argon. However, an operating gas mixture of an inert gas and a reactive gas can be used for coating. One such operating gas is, for example, argon and nitrogen, so that nitride layers can be deposited on the objects.

- 25           The gas flow can be adjusted to a minimum of  $10 \text{ cm}^3/\text{min}[\text{STP}]$  (cubic centimeters per minute at standard temperature and pressure) and a maximum of  $1000 \text{ cm}^3/\text{min}[\text{STP}]$ .

If only a very small coating or no coating at all is intended to be applied, the potential difference between the plasma and the box structure should be set to be under 200 V and/or the pressure should be increased by at least a factor of three.

- 30           With adjustment of this kind a surface modification, as already noted in general, can be carried out.

The device in accordance with the invention can also be used to produce composite structures. For this it is provided that a solid powder is supplied through one of the openings that are present or through an opening specifically made for this. It is also possible to place the solid powder in the device in a container. The particles  
5 of the solid powder preferably have a size from  $10^{-4}$  to  $10^{-9}$  m. Basically all known hard materials are possibilities as solid particles. Examples are high-melting metal oxides like corundum or titanium oxide. Diamond graphite or nitrides can also be used. In accordance with the method, when the powder is introduced via an opening, it is mixed into the inert gas stream. If the powder is supplied in a container,  
10 automatic turbulent mixing takes place due to the applied vacuum. The particles are then deposited on the surface that is to be coated.

The mode of operation in accordance with the invention will be described first below, in general form and then in more detail using two specific examples.

After putting the objects in the box structure, the box structure or the  
15 surrounding vacuum chamber is evacuated out by means of a vacuum pump and at the same time or shortly afterwards flushing with the operating gas is carried out.

If a sufficiently low pressure (1-10 mbar) has been achieved, the box structure is charged to a negative potential with respect to the plasma and the glow discharge is initiated by the supply of energy. The ion-supported desorption of the  
20 adsorbate layers takes place by means of this.

After sufficient cleaning the pressure is reduced to a pressure in the range between 0.001 and 1 mbar by reducing the feed of operating gas and the potential difference between the box structure and the plasma is increased. This can take place, for example, by increasing the negative potential, thus a higher negative  
25 voltage is supplied to the box structure. Due to this, material of the coating material is stripped from the inner wall of the flat structure and the objects in the structure are correspondingly coated. In each case according to the coating to be applied a pure inert gas or an inert gas-reactive gas mixture can be used as the operating gas. The fraction of reactive gas, however, must be established in correspondence with the  
30 desired layer structure.

Then the glow discharge can be switched off, the supply of operating gas in the pump disconnected and the vacuum chamber or the box structure flooded and after opening the box the modified or coated objects are removed.

The following Examples 1 and 2 are intended to describe on the one hand  
5 coating of objects with copper and on the other coating with titanium nitride in more specific detail.

#### Example 1

The objects are put into the box structure, which is shaped as a tube, is  
10 situated in a vacuum vessel, and consists of block copper. For evacuation of the vacuum vessel the vacuum pump is connected. At the same time flushing with argon at about  $100 \text{ cm}^3/\text{min}[\text{STP}]$  is carried out.

Upon reaching a pressure of 5 mbar the box structure is charged to a negative potential of 300 V compared to a rod shaped anode inserted into the box structure  
15 and the glow discharge is initiated. This causes the ion-supported desorption of the adsorbate layers from the inner wall of the box structure.

After sufficient cleaning the pressure is reduced to the operating pressure of 0.5 mbar by reducing the feed of gas and the potential of the box structure is set to – 500 V, so that coating of the objects with copper takes place.

20 After 10 min coating time the glow discharge is switched off by disconnecting the supply of current and the argon supply is turned off. The pump is disconnected and the box structure is aerated. The vacuum vessel and box structure are opened and the coated objects are removed.

#### 25 Example 2

The objects are put into the box structure. The box has the shape of a rectangular parallelepiped, consists of aluminum and is itself the vacuum vessel, which is coated nearly completely on its inside with titanium sheets ("targets"). The box structure has a short tubular stub in its wall, to which a microwave source is  
30 connected.

The vacuum pump is switched on for evacuation of the box. Shortly after that argon is supplied for flushing at about  $300 \text{ cm}^3/\text{min}[\text{STP}]$ . Upon reaching a pressure of 10 mbar the box structure is charged to a negative potential of 250 V and the glow discharge is initiated by turning on the microwave source.

5        After 3 min cleaning the pressure is reduced to 0.3 mbar by reducing the gas supply, and the objects are supplied with a potential of  $-500 \text{ V}$ , through which surface cleaning takes place. Then 10% nitrogen is added to the argon and the potential of the box structure is set to  $-600 \text{ V}$ , so that coating of the objects with titanium nitride takes place.

10       After 15 min of coating the glow discharge is turned off and the operating gas supply stopped. The pump is isolated by a valve and the box is aerated. The box is opened and the objects are removed.

The organization of possible examples of a device in accordance with the invention is described in more detail below.

15       Here:

Figure 1 shows an example of a device in accordance with the invention with an inserted electrode for plasma generation, and

20       Figure 2 shows a second example of a device in accordance with the invention with an opening through which microwaves can be directed for plasma generation.

Figure 1 represents a box structure 1 with rectangular cross section. An end face 8 is formed as an opening through which objects 2 are introduced and can be removed. Opening 8 can, as shown, be reclosed. The operating gas can be introduced into the flat structure 1 through opening 3 and can be removed again  
25       through the larger and diametrically oppositely arranged opening 4.

Electrode 5, which is in this case connected as an anode, is inserted via an additional opening 6'. Between anode 5 and the box structure 1 there is insulation, not shown, so that the potentials are separate from one another.

30       Figure 2 shows a cylindrical box structure 1, in which again several objects 2 are arranged on a support 7 insulated from the box structure 1. The upper face is again formed as a cover 8, which can be removed and reattached.

In this example there are two openings 3 in the outer jacket surface, through which operating gas can be introduced into the interior of the box structure 1. The gas can be removed through opening 4, which in this example is combined with a support, from the box structure 1.



### Claims

1. A device for coating and/or surface modification of objects in a vacuum, by means of a plasma, which is characterized by the fact that a box structure (1) of an electrically conductive material forms a vacuum chamber or can  
5 be inserted into a vacuum chamber, into which objects (2) are inserted into the box structure (1) through at least one closable opening (8) at a distance from the inner wall, at least one opening (3) for supply and at least one opening (4) for removal of operating gas and an opening (6,6') for introduction of energy for generation of a glow discharge are present, and the box structure (1) has a potential that is  
10 electrically negative with respect to the plasma generated by the glow discharge.

2. A device as in Claim 1, which is characterized by the fact that an electrode (5), to which a DC or AC voltage is applied for plasma generation, is inserted into the box structure (1) through an opening (6').  
15

3. A device as in Claim 1, which is characterized by the fact that microwaves for plasma generation are directed into the interior of the box structure through opening (6).

20 4. A device as in one of Claims 1-3, which is characterized by the fact that the objects (2) are arranged in electrically isolated fashion from the box structure (1).

5. A device as in one of Claims 1-4, which is characterized by the fact  
25 that the objects (2) are supplied with a settable electrical potential.

6. A device as in one of Claims 1-5, which is characterized by the fact that the inner wall of the box structure (1) or the box structure (1) is formed of a coating material or is arranged there as a flat target.  
30

7. A device as in one of Claims 1-6, which is characterized by the fact that the box structure (1) is cooled.

8. A device as in one of Claims 1-7, which is characterized by the fact that the clear width of the box structure (1) is at least 1.2 times that of the objects (2) and the objects (2) fill the space available in the box structure (1) to a percentage of 0.1% to 30%.

9. A device as in one of Claims 1-8, which is characterized by the fact that the size of the withdrawal opening (5) is larger than the sum of the larger of the other openings (3,6,6') of the box structure (1).

10. A device as in one of Claims 1-9, which is characterized by the fact that the box structure (1) or its inner surface consists of a metal, a metal alloy or a metal compound.

11. A method for coating and/or modification of the surfaces of objects with a device as in one of Claims 1-10, which is characterized by the fact that after evacuation to a sufficiently low pressure and flushing with an operating gas a plasma is generated in the box structure (1), where the plasma power and the negative potential of the box structure (1) are set so that modification of the surface and/or, through material stripping from the inner wall of the box structure (1), coating of the surface of the object (2) is carried out.

12. A method as in Claim 11, which is characterized by the fact that before modification or coating an ion-supported desorption of deposited adsorbate layers is carried out with applied negative potential applied to the box structure (1) and glow discharge initiated.

13. A method as in Claim 11 or 12, which is characterized by the fact that reactive gas is supplied during the coating.

14. A method as in one of Claims 11-13, which is characterized by the fact that solid powder is introduced into the box structure and/or is made available in a container arranged there and the solid powder is deposited on the surface (2) of the objects.

15. A method as in one of Claims 12-14, which is characterized by the fact that the potential difference between the box structure (1) and the plasma is set in the range between 100-1000 V.

16. A method as in one of Claims 12-15, which is characterized by the fact that the operating gas is adjusted to a volume flow of  $10-1000 \text{ cm}^3/\text{min}[\text{STP}]$ .

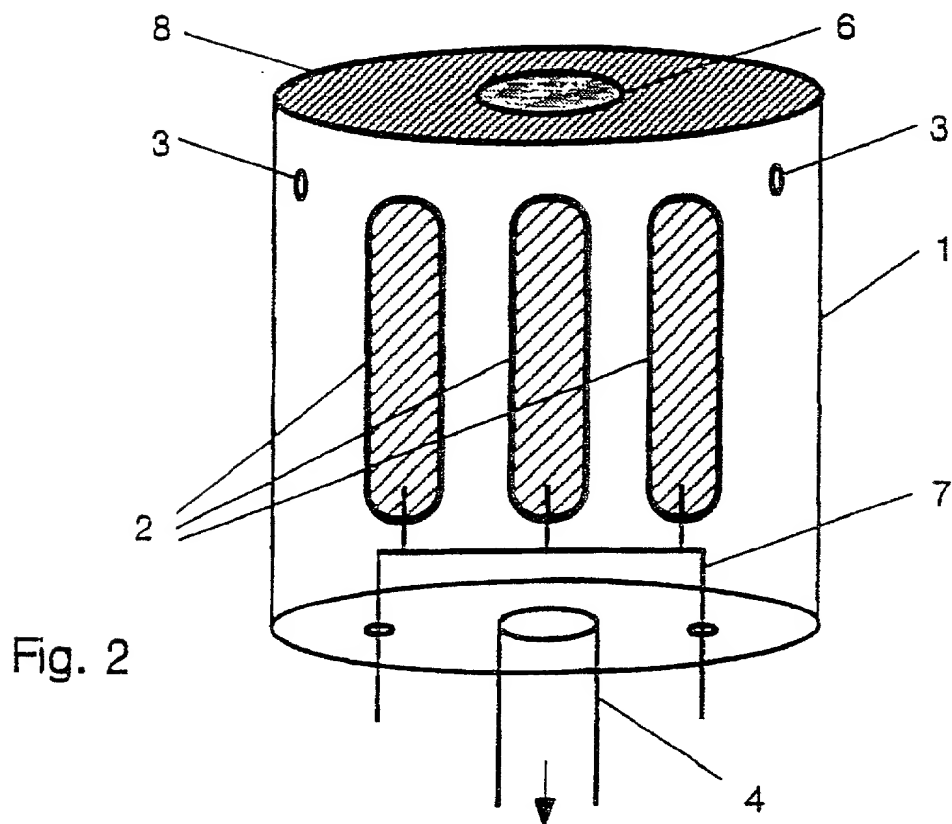
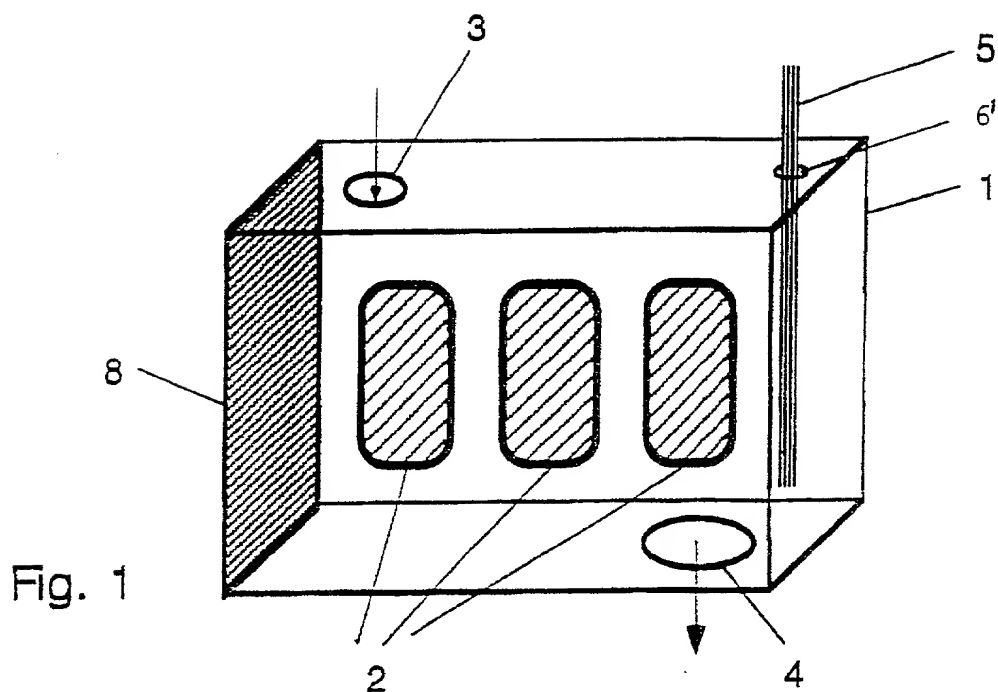
17. A method as in one of Claims 12-16, which is characterized by the fact that for surface modification the potential difference between the plasma and the box structure (1) is adjusted to less than 200 V and/or the pressure is increased by at least threefold.

18. A method as in one of Claims 12-17, which is characterized by the fact that a hollow cathode flow discharge is formed in the box structure (1).

19. A method as in one of Claims 11-18, which is characterized by the fact that an inner gas, reactive gas or a mixture of inert and reactive gas is introduced in a timewise defined fashion as the working gas into the box structure (1).

### Summary

The invention concerns a device and a method for coating and/or surface modification of objects in a vacuum using a plasma, where there is the possibility of coating or modifying variform objects on all sides without a large expense for plant or process engineering being necessary. In accordance with the invention, a box structure (1) of an electrically conductive material that forms a vacuum chamber or can be inserted into a vacuum chamber is used. Objects (2) can be introduced into the box structure to at least one closable opening (8) at a distance from the inner wall. In addition, there are at least one opening (3) for supply and at least one opening (4) for removal of the operating gas as well as one opening (6,6') for introduction of energy for generation of a glow discharge and the box structure (1) has a potential that is electrically negative with respect to the plasma generated by the glow discharge.



Docket No.  
65,243-001

# Declaration and Power of Attorney For Patent Application

## English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

DEVICE AND METHOD FOR THE VACUUM PLASMA PROCESSING OF OBJECTS

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on January 10, 2001 as United States Application No. or PCT International Application Number 09/743,545 and was amended on \_\_\_\_\_

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

<u>198 34 733.2</u>	<u>GERMANY</u>	<u>31/July/1988</u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
_____	_____	_____	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
_____	_____	_____	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

PCT/EP99/05409

28/July/1999

Pending

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

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